

REMARKS/ARGUMENTS

With entry of the foregoing amendment, the claims in the application are: 1, 2, 4 5, 10, 11 and 12.

New Claim 12 is presented in order to make certain that all aspects of applicants' invention are claimed. Notwithstanding the fact that all of the other claims remaining in the application specify the method of compaction, applicants respectfully submit that the subject matter of Claim 12 is patentable over the prior art of record in the parent application without being limited to the method by which the silica is compacted.

In the parent application, the Examiner relied on the following references:

Klinge (US 4,877,595) under 35 U.S.C. § 102(b)

Burger (US 4,680,173) under 35 U.S.C. § 102(b)

Degussa (EP 0808 880 A2) with the US equivalent of *Hartmann* (US 5,959,005) under 35 U.S.C. § 102(b).

In the parent application, the Official Action alleged that the silica of *Klinge* was pyrogenically produced and made hydrophobic with a silane that is halogen free. In col. 4, line 12, *Klinge* identifies his silica as "Aerosil R972". However, applicants provide herewith a copy of Degussa Technical Bulletin No. 63, pg. 6, para. 2.2.1, which discloses that the silica identified as Aerosil R972 is made with dimethyl dichlorosilane, i.e., a silane that is not halogen-free.. Also, enclosed is a copy of Degussa Technical Bulletin No. 54, pg. 5, which shows the structure

of Aerosil R972 and, further, that it is produced with a halogen-containing silane, namely, dimethyl dichlorosilane, see, lines 2 and 3.

Hence, applicants have established that *Kling*'s silica is not produced by reaction with a halogen-free silane, as called for by the claims in this application. It follows that *Kling* cannot be an anticipation of the claimed invention.

In the parent application, the Official Action also indicated that there was confusion as to the correct name of the silane used by *Kling*. Again, reference is made to the accompanying Degussa Technical Bulletin Nos. 54 and 63, which clearly show that the *Kling* R972 silica is made using a halogen-containing silane.

Accompanying this response is a copy of the Degussa Technical Bulletin No. 63, fig. 9, which is a graph showing comparative data demonstrating the unexpected difference in the performance of the silica which is made with a halogen-free silane (R202) and the R972 silica which are made with a halogen-containing silane. Note the very large difference in viscosity and extrusion rate showing a much lower viscosity and much higher extrusion rate for the silica (R202) made with a halogen-free silane. Additionally, applicants would comment that a silica is hydrophobized with a halogenated silane shows a carbon content of less than 1.3 percent. This is shown by the table on page 33 of Degussa Technical Bulletin No. 63, showing the highlighted values for Aerosil R972 and R974.

In comparison, when the silica is made hydrophobic by reaction with a non-halogenated silane, the silica demonstrates a carbon content that is much higher. See, for example, the values for R202 (3.5-5.0%), R805 (4.5-6.5%) and R812 (2.0-3.0%).


In the Degussa Technical Bulletin No. 63, Table 15, relates to storage stability of resins containing silica in terms of viscosity and extrudability. The data shows that polymers containing silicas R972 and R974 produced with halogenated silane display a higher viscosity, lower extrudability and greater sag than do polymer products with the non-halogenated silicas, R202, R805, R812S and R812. The non-halogenated surface modified silicas show an excellent anti-sag behavior. See, Table 15.

Thus, the data presented shows that the silicas made with halogen-free silanes and polymer products containing them are unexpectedly different from the silica made with halogen containing silanes and polymer products containing them. These differences in behavior could not have been foreseen or predicted from the prior art of record.

Examination on the merits is awaited.

Respectfully submitted,

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2.1 Hydrophilic silicas

2.1.1 Standard AEROSIL products

AEROSIL is a very light, bluish-white powder formed from very fine, spherical primary particles. Although these particles are amorphous, they do not occur in isolation adjacent to one another but aggregate and agglomerate to form larger configurations. Their average diameters range from 7 to 40 nanometres. Since the particles are so small, they result in an extremely high specific surface area which is usually determined by the nitrogen adsorption method based on BRUNAUER, EMMETT and TELLER (the „BET“ method) and which, depending on production parameters, may be between 50 m²/g and 380 m²/g. The surface of AEROSIL particles is relatively smooth, consisting of the boundary surface of a spatial network of siloxane groups (-Si-O-Si-). Silanol groups are also located on the surface of silica particles. As moisture can be adsorbed at these points, silicas such as AEROSIL are normally hydrophilic and hence can be wetted with water. Further details are contained in Publication No. 11 of the Technical Bulletin series. In most instances, hydrophilic AEROSIL types with specific surfaces between 130 m²/g and 380 m²/g are used in sealants, depending on the polymer system and the desired effect.

2.1.2 Precipitated silicas

Manufacture and properties of the various processes are described in Publication No. 32 of the Technical Bulletin series. The crucial difference between precipitated silicas and the AEROSIL types is their purity. For example, the drying and ignition loss value of precipitated silicas, app. 5 % by weight, is about three times greater than that of AEROSIL. The silanol-group densities in precipitated silicas are also higher than in the AEROSIL types. Another important difference is that, because of their more pronounced agglomerate formation, most commercially available precipitated silica types are ground, whereas all AEROSIL types are left unground.

2.2 Hydrophobic silicas

Hydrophobic silicas are always after-treated products. After-treatment processes can be performed by using either the different types of AEROSIL or the various types of precipitated silicas.

2.2.1 AEROSIL „R types“

AEROSIL R 972 has been commercially available since 1962 and is the oldest chemically aftertreated synthetic silica, i.e. the first hydrophobic product on the market. Unlike silicas which are naturally hydrophilic, hydrophobic types are not wetted by water. Although the hydrophobic silicas' density is greater than water, they float on the surface of water. In the case of AEROSIL R 972, chemically bonded dimethyl silyl groups are produced at the silica surface as a result of binding the hydrophilic silanol groups with dimethyl dichlorosilane. Other hydrophobic AEROSIL types have now become available commercially and are designated by an „R“. This „R“ stands for „repellent to water“. They differ in their specific surface area and the organic groups located on the silica surface. AEROSIL R 974 differs from AEROSIL R 972 by virtue of its higher BET surface.

In terms of the geometrical surface area, AEROSIL R 812 can be compared with AEROSIL 300, but has trimethyl silyl groups on the silica surface. In principle, every hydrophilic AEROSIL type can be modified by dimethyl silyl or trimethyl silyl groups. Appropriate test products were also produced for comparison purposes. Of all the hydrophobic AEROSIL types, AEROSIL R 202 has the lowest BET surface of 100 m²/g and is after-treated with a polydimethyl siloxane. AEROSIL R 805 is rendered hydrophobic by means of a silane with a fairly long chain organic group, e.g. an octylsilane. Hydrophobizing substantially reduces the amount of moisture that is absorbed by hydrophilic silicas, cf. Figure 1. For example, AEROSIL R 974, even at a relative air humidity of 80 %, adsorbs just 0.5 % water, whereas the hydrophilic AEROSIL 200 with a comparable surface area absorbs some 10 times more.

Viscosity and sag behaviour

Figure 7 shows that there is no correlation between viscosity and sag behaviour, i.e. the sealant can still sag even with a very high viscosity. This also applies to high filler additives based on natural products, which can be used to obtain high viscosities but not thixotropic properties.

Flow limit and sag behaviour

Figure 8 compares the flow limits of different samples from Table 15 with sag behaviour measurement values. The flow limits were ascertained here by means of a cone-and-plate rheometer based on Casson's regression model. It can be seen that the flow limit correlates well with the sag behaviour. It is therefore possible to use the flow limit to quantify sag behaviour.

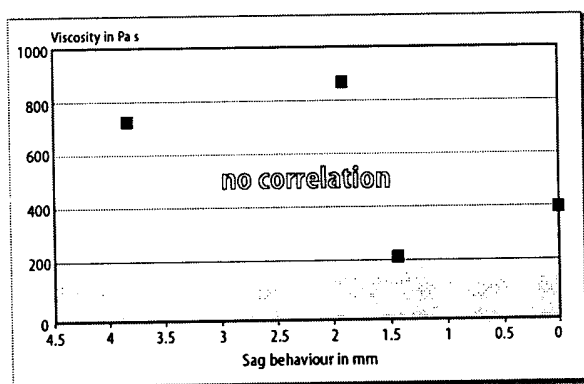


Figure 7: Correlation viscosity versus sag behaviour.

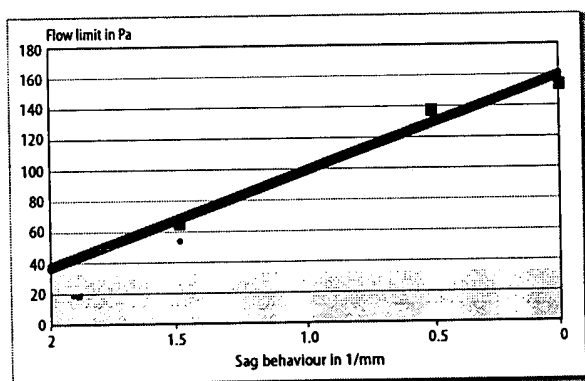


Figure 8: Correlation flow limit versus sag behaviour.

Viscosity and extrudability

Figure 9 shows that there are significant correlations between viscosities and extrudability rates. The higher the compound's viscosity, the lower the extrudability.

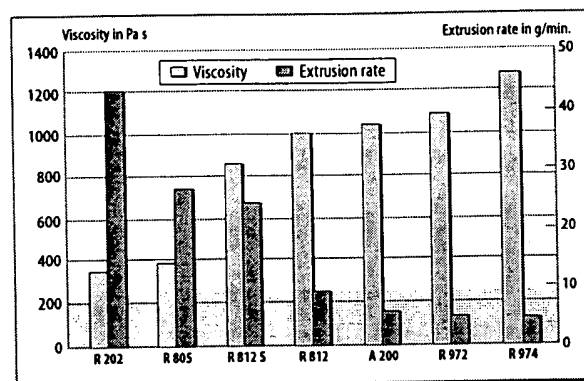


Figure 9: Viscosity and extrudability.

5.2.3 Storage stability

Storage stability is generally defined as the ability to maintain constant rheological properties in the sealant throughout a specific period, i.e. the sealant's viscosity or extrudability do not increase or decrease substantially during storage. Constant rheological properties over several months are very important, as otherwise it is no longer possible to process sealants satisfactorily. Table 15 shows the measured viscosities, extrudabilities and the sag behaviours of the polysulphide sealants thixed with AEROSIL and precipitated silicas after being stored at room temperature for 16 weeks.

With regard to the sag behaviour, all thixed polysulphide sealants show good to excellent storage stabilities with exception of the thixed sealants using AEROSIL 200, AEROSIL R 972 and AEROSIL R 974. Especially in the case of the thixed sealants using SIPERNAT D 10 and Sipernat 383 DS the adjusted sag behaviour remained constant even after being stored for 16 weeks.

Silica	parts	Viscosity in Pa s (5 rpm)		Extrudability in g/min		Sag behaviour in mm	
		1 day	16 weeks	1 day	16 weeks	1 day	16 weeks
without	—	8	1	100	-	down	down
AEROSIL R 202	5	419	392	55	46	0	1.0
AEROSIL R 805	7	474	424	32	29	0.5	1.5
AEROSIL R 812 S	9	922	831	28	22	0	1.0
AEROSIL R 812	10	1088	945	10	12	0.5	1.0
AEROSIL R 972	14	1082	915	7	7	3.0	4.5
AEROSIL R 974	13	1306	1120	6	7	1.5	4.0
AEROSIL 200	12	953	812	6	4	0.5	4.0
Sipernat D 10	27.5	800	880	4	6	0	0
Sipernat D 17	20	819	864	9	10	0	1
Sipernat 320 DS	15	1024	910	12	12	0	1
Sipernat 383 DS	13	1306	1290	14	14	0	0
Sipernat 500 LS	11.5	998	815	12	11	0	1

Table 15: Storage stability of polysulphide sealants thixed with various silicas.

5.2.4 Reinforcing properties of AEROSIL and precipitated silicas

Even if the function of AEROSIL and precipitated silicas is most significant in silicone compounds, considerable improvements in the mechanical properties were found in other sealants.

Table 16 indicates the mechanical properties of various AEROSIL types and precipitated silicas in polysulphide sealants tested in

the previous section. A point of interest is that on the basis of all silicas tested with different loadings, mechanical properties of relatively even quality are obtained in the short-chain test polymer LP 977. As the proportion of filler rises, higher tear resistance achieved.

Table 17 shows another example of how to improve the mechanical properties of a 1K polysulphide sealant filled with chalk by adding AEROSIL.

Silica	parts	Tear strength [N/mm]	Resilience [%]	Shore-A-Hardness
AEROSIL R 202	5	3.4	54	49
AEROSIL R 805	7	3.9	52	51
AEROSIL R 812 S	9	4.7	46	47
AEROSIL R 812	10	4	50	51
AEROSIL R 972	14	5.9	48	55
AEROSIL R 974	13	5.6	48	51
AEROSIL 200	12	6.6	49	55
Sipernat D 10	27.5	8.1	40	61
Sipernat D 17	20	6.1	40	48
Sipernat 320 DS	15	5.0	44	51
Sipernat 383 DS	13	5.0	47	54
Sipernat 500 LS	11.5	4.4	45	48

Table 16: Mechanical properties of polysulphide sealants with various silicas.

Formulation	Modulus 100 [N/mm ²]	Tensile strength [N/mm ²]	Elongation at break [%]	Tear resistance [N/mm]	Shore-A- Hardness
1) Winnofil S AEROSIL 130	0.3	1.1	1000	4.3	15
2) Winnofil S AEROSIL 130	0.4	1.6	1000	5.6	21
3) Omya BSH AEROSIL 130	0.2	0.7	900	3.6	13
4) Omya BSH AEROSIL 130	0.4	1.4	900	5.5	23

Table 17: Improving mechanical properties of a vulcanised 1-component polysulphide sealant with different calcium carbonate fillers by adding AEROSIL (test formula 8.1.3).

Hydrophobic AEROSIL

Test method		AEROSIL R 972	AEROSIL R 974	AEROSIL R 202	AEROSIL R 805	AEROSIL R 812	AEROSIL R 812 S	AEROSIL R 104	AEROSIL R 106	AEROSIL R 8200	AEROSIL R 816	Titandioxid T 805
Behaviour with respect to water		hydrophobic										
Appearance		loose white powder										
BET-surface area ¹⁾	m ² /g	110±20	170±20	100±20	150±25	260±30	220±25	150±25	250±30	160±25	170±25	45±10
Average primary particle size	nm	16	12	14	12	7	7	12	7	12	12	21
Tapped Density ²⁾												
Standard Material	g/l	50	50	50	50	50	50	50	50	140	40	200
Compacted Material	g/l	90	90					90				
Moisture ³⁾ (2 hours at 105 °C) at leaving plant site	%	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 1.0	< 1.0
Ignition loss ^{4) 7)} (2 hours at 1000 °C)	%	< 2	< 2	4 - 6	5 - 7	1.0 - 2.5	1.3 - 3.0	1.0 - 2.5	1.0 - 2.5	2.5 - 3.5	2.0 - 4.0	< 5.0
Carbon content	%	0.6 - 1.2	0.7 - 1.3	3.5 - 5.0	4.5 - 6.5	2.0 - 3.0	3.0 - 4.0	1.0 - 2.0	1.5 - 3.0	2.0 - 4.0	1.2 - 2.2	2.7 - 3.7
pH value ^{5) 10)}	%	3.6 - 4.4	3.7 - 4.7	4 - 6	3.5 - 5.5	5.5 - 7.5	5.5 - 7.5	> 4.0	> 3.7	> 5.0	4.0 - 5.5	3.0 - 4.0
SiO ₂ ⁸⁾	%	> 99.8	> 99.8	> 99.8	> 99.8	> 99.8	> 99.8	> 99.8	> 99.8	> 99.8	> 99.8	< 2.500
Al ₂ O ₃ ⁸⁾	%	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05		< 0.05	
Fe ₂ O ₃ ⁸⁾	%	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.010
TiO ₂ ⁸⁾	%	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	> 97.00
HCl ¹¹⁾	%	< 0.05	< 0.1	< 0.025	< 0.025	< 0.025	< 0.025	< 0.02	< 0.025	< 0.025	< 0.025	
Packaging (net/weight) ¹²⁾	kg	10	10	10	10	10	10	10	10	15	10	20

¹⁾ in acc. to DIN 66131

²⁾ in acc. to DIN ISO 787/XI, JIS K 5101/18 (not sieved)

³⁾ in acc. to DIN ISO 787/II, ASTM D 280, JIS K 5101/21

⁴⁾ in acc. to DIN 55921, ASTM D 1208, JIS K 5101/23

⁵⁾ in acc. to DIN ISO 787/IX, ASTM D 1208, JIS K 5101/24

⁷⁾ based on material dried for 2 hour at 105 °C

⁸⁾ based on material ignited for 2 hours at 1000 °C

¹⁰⁾ in Water: methanol = 1 : 1

¹¹⁾ HCl content is part of the ignition loss

¹²⁾ AEROSIL V-Grades will be delivered in paperbags of 15 kg

The data have no binding force. Any parameter should be specified individually if necessary.

AEROSIL can be surface-modified by reacting the silanol groups with suitable compounds such as silanes. AEROSIL R 972 is obtained by reaction with dimethyl dichlorosilane, for example; this product exhibits chemically bound dimethyl silyl groups on its surface and can no longer be wetted with water – in other words, it is hydrophobic.

AEROSIL R 972 became the first hydrophobic silica to be manufactured on an industrial scale in 1962. Further hydrophobic AEROSIL types are now available, produced by similar industrial-scale methods using corresponding silanes. Figure 3 provides a summary of these and highlights the difference between them and hydrophilic AEROSIL types according to the schematically represented surface groups. All hydrophobic AEROSIL types carry the suffix „R“ to indicate their water-repellent character.

Hydrophilic and hydrophobic AEROSIL have proven effective for numerous areas of application. In view of their use in the plastics industry, the principal properties of fumed silicas are listed below:

- Reinforcing fillers
- Thickening and thixotropic agent for resins
- Anti-sedimentation agent for cast resins and adhesives
- Free flow aid for powder coatings

In contrast to silicas of mineral origin, meaning quartz powder which is used mainly as a „filler“ in the true sense of the word, the desired effects can be obtained by adding only relatively small amounts of synthetic silicas.

A summary of the applications of AEROSIL in general and for plastics in particular is given in [2] and [3].

Since the application-relevant properties of a silica can be optimized for specific applications via the type of surface modification, AEROSIL R 202 and AEROSIL R 805 were developed.

Theoretical considerations have led to the supposition that longerchain, hydrophobic groups in certain liquid polymer systems – particularly vinyl ester and epoxy resins – ought to make it possible to control the rheological properties more effectively. AEROSIL R 202, with a surface on which polydimethyl siloxane groups are fixed, and AEROSIL R 805, which is rendered hydrophobic with octyl groups, fulfil these expectations to a remarkable degree.

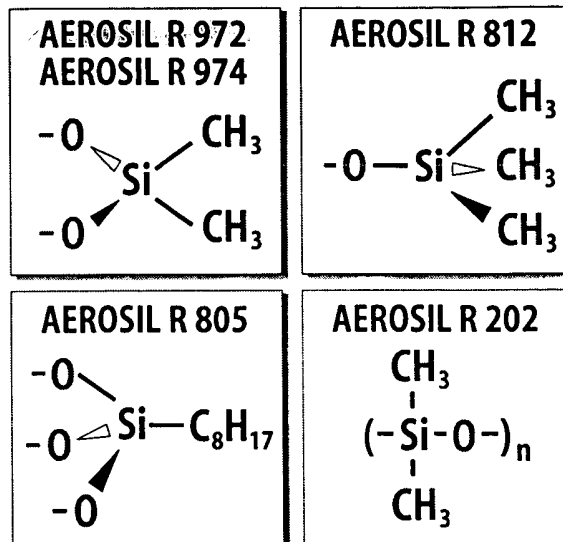


Figure 3: Hydrophobic AEROSIL types and their surface groups

4. Vinyl Ester Resins

The UP resins Palatal P 4,-P 5,-A 410 and the styrene-free test product Palatal M 671 -01V have been used for tests to date.

In contrast to conventional UP resins, the thickening of vinyl ester resins with AEROSIL 200 presents problems, since the hydrophilic AEROSIL aggregates are wetted to a greater degree as a result of the larger number of hydroxyl groups in vinyl ester resins, and the thickening and thixotropic effect is therefore too low [12].

The hydrophobic silica AEROSIL R 202 solves this problem, as illustrated by the two different vinyl ester resins Palatal®, A 430 (DSM resins, Zwolle, Netherlands) and Derakane®, 411 -45 (Dow Deutschland Inc., 77836 Rheinmunster, Germany) (Figures 28 and 29).

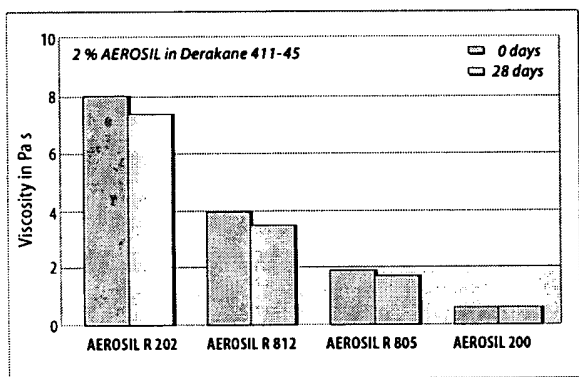


Figure 28: Comparison of the thickening effect and storage stability of various AEROSIL types in a vinyl ester resin (40% styrene content).

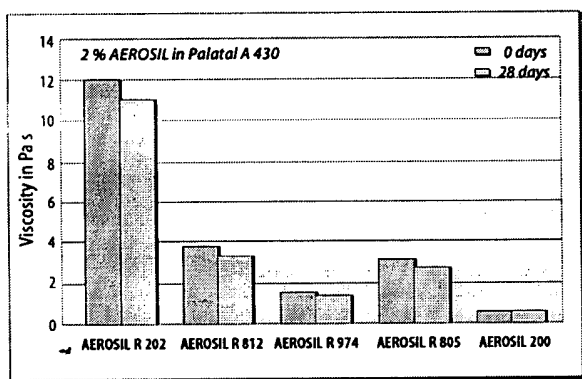


Figure 29: Comparison of the thickening effect and storage stability of various AEROSIL types in a vinyl ester resin (45% styrene content).

5. Formula Questions

5.1 Laminating Resins and Gelcoats

For thickening laminating resins, concentrations of between 0.7 and 1.3% AEROSIL are used. Gelcoats are normally always thickened and generally contain between 2.0 and 2.5% fumed silica, or in special cases up to 4.0%. The exact percentage of silica depends on the desired rheological properties and the composition of the laminating resins and gelcoats.

Gelcoats moreover contain pigments, and possibly fillers such as talc, dispersing agents and deaeration additives, and are diluted to a monomer content of approx. 40-50% with styrene and/or other monomers, depending on rheological requirements [14].

Simple guideline formulae for laminating resins and gelcoats are given in Section 6.

Before processing, accelerator solution (e. g. approx. 1 % cobalt octoate, potassium octoate or dimethyl aniline solution) and peroxide solution (e.g. approx. 2% methyl ethyl ketone peroxide solution) are added to the laminating resin and gelcoat, according to the desired reactivity. Pre-accelerated systems are likewise commercially available.

5.2 Influence of Formula Ingredients

The choice of medium in which to disperse the AEROSIL 200 is of considerable importance for the rheological properties and storage stability of the thickened UP resins.

In order to demonstrate the influence of the dispersing sequence by way of an example, the following variations in the incorporation of AEROSIL were tested:

1. UP resin + AEROSIL 200 (0.5%) dispersed with dissolver; then styrene added.
2. UP resin + styrene + AEROSIL 200 (0.5%) dispersed with dissolver.
3. Styrene + AEROSIL 200 prepared in mixer (5 % conc.), stored overnight; then UP resin added with dissolver.
4. Styrene + AEROSIL 200 dispersed for 6 h in a ball mill (5 % conc.); then UP resin added with dissolver.

The results are summarised in Table 2.